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Liquid Crystal Materials for Laser Beam Steering

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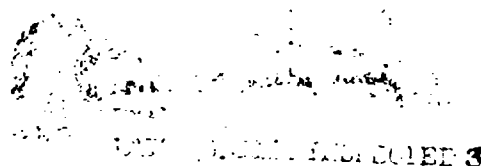
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13. ABSTRACT (maximum 200 words) Several new liquid crystal compounds have been developed for laser beam steering application. The asymmetric dialkyl diphenyl-diacetylenes exhibit a low melting temperature, wide nematic range, high birefringence, low viscosity and small heat fusion enthalpy. They are excellent host materials for forming eutectic mixtures except for the small dielectric anisotropy. To enhance dielectric anisotropy, some polar diphenyl-diacetylenes and tolans, and a new series of the nitro-azo-benzene dyes have been considered. Among these polar compounds, the nitro-azo-benzene dyes exhibit a mesogenic phase with melting temperature at about 80°C, huge dielectric anisotropy, excellent solubility and relatively low viscosity. The solubility and viscosity of these dyes are about one order of magnitude better than the commonly employed commercial dyes. Adding 5% of this dye to an asymmetric diphenyl-diacetylene binary mixture reduces its threshold voltage from 3.5 to 1.7 V _{rms} .				
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1.0 INTRODUCTION

For steering laser beams using a nematic liquid crystal (LC) phase modulator, the following LC properties are highly desirable: (1) high birefringence (Δn), (2) small visco-elastic coefficient (γ_1/K_{11}), (3) large dielectric anisotropy ($\Delta\epsilon$), (4) wide nematic range, (5) small absorption, and (6) good thermal and photo-stability.

Among these parameters, high Δn plays the most important role. It enables a large phase shift to be achieved using a thin LC layer, which in turn, results in a faster response time. High Δn also leads to a wide scanning angle, and improves the beam deflection efficiency. Small γ_1/K_{11} also contributes to fast response time. Large $\Delta\epsilon$ contributes to lowering the operation voltage, and subsequently reduces the cost of the associated driving electronics. Wide nematic range is essential if the LC device is to be operated or stored in a wide temperature range. Small absorption is particularly important for IR application where some molecular vibrational absorption bands exist. A smaller absorption implies a lower optical loss. Finally, good thermal and photo-stability assures a long device lifetime. For practical laser beam steering application, the aforementioned properties have to be satisfied simultaneously.

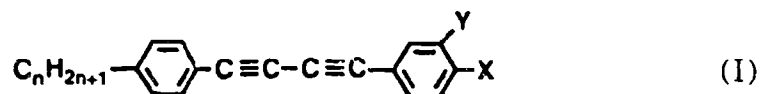
Many LCs with high Δn are often associated with a high viscosity as well. The LC birefringence is primarily determined by the molecular conjugation length and the anisotropy of electronic transitions. On the other hand, viscosity is determined by the activation energy, molecular weight and shape (or moment of inertia), and temperature. A longer conjugation length leads to a higher Δn , however, its moment of inertia also increases resulting in a higher viscosity. Thus, a low molecular weight, linearly conjugated LC molecule is preferred from the high Δn and low viscosity standpoints.

2.0 NEW LC MATERIALS

During the course of this contract effort, we have discovered three series of new LC compounds which exhibit both high Δn and low viscosity. These new LCs were synthesized by Prof. L. R. Dalton's group (a parallel AFOSR contract) at the University of Southern California. In addition, some new LC samples were generously donated by Prof. C. S. Hsiao's group from the National Chiao Tung University (Taiwan), and by Prof. B. M. Fung's group from the University of Oklahoma. The three new LC series we studied in this contract are: 1. Diphenyl-diacetylenes, 2. Tolanes, and 3. LC dyes

2.1 Diphenyl-diacetylene (PTTP) Series

A general structure of the diphenyl-diacetylene (abbreviated as PTTP; P stands for a phenyl ring and T for a triple bond) LC is shown as following:



where X can be an alkyl ($\text{C}_m\text{H}_{2m+1}$) or a polar group (e.g., CN, F or Cl), and Y can be an hydrogen (H) or a polar group (F or Cl). About 60 PTTP LC compounds have been synthesized and their physical properties evaluated (see publication list #1 to 4 in Sec. 5). Some representative homologs are listed in Table 1 for comparison.

Table 1 Phase transition temperatures (in °C), birefringence (Δn), dielectric anisotropy ($\Delta\epsilon$) and heat fusion enthalpy (ΔH , in kcal/mol) of some dialkyl and polar PTTP homologs.

PTTP-	Phase Transition				Δn	$\Delta\epsilon$	ΔH
24	K	43.6	N	97.7	0.35	0.8	2.47
33	K	107.5	N	131.9			6.00
36	K	41.5	N	97.5			2.91
46	K	24.9	N	79.7			4.84
55	K	86.0	N	111.3			4.60
6CN	K	(144.0)	N	145.3	0.44	17	8.06
6Cl	K	112.9	I		0.35	6	6.87
4F	K	85.4	N	87.7	0.31	5.2	6.00
6FF	K	(48.5)	N	65.3	0.28	7.8	5.95

From Table 1, the asymmetric dialkyl PTTPs exhibit a much lower melting point, wider nematic range and smaller heat fusion enthalpy than their corresponding symmetric homologs with the same chain length. For example, the melting point of PTTP-24 is ~64 degrees lower than that of PTTP-33, and PTTP-46 is ~40 degrees lower than PTTP-55. A low melting temperature and small ΔH are important for formulating eutectic mixtures with a low melting point. The PTTP-nm homologs are excellent host candidates for forming eutectic mixtures except that their dielectric anisotropy is small ($\Delta\epsilon \sim 0.8$). Therefore, for practical applications some polar dopants have to be added in order to enhance the dielectric anisotropy.

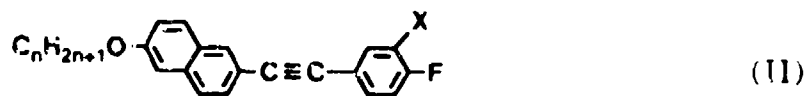
Three types of polar groups have been investigated: cyano (CN), fluoro (F) and chloro (Cl). From Table 1, the CN group indeed greatly enhances the dielectric anisotropy due to its large dipole moment. However, the melting temperature of PTTP-6CN is too high, nematic range too narrow and ΔH too large so that its solubility to the host material is quite limited. By contrast, PTTF-6Cl exhibits no mesogenic phase at all. The fluorinated PTTPs have a slightly lower birefringence than PTTP-nm owing to the strong electro-negativity of the fluoro group. The electronic resonance wavelength of the fluoro compound is shorter than its corresponding dialkyl homolog resulting in a lower birefringence.

The PTTP-nF homologs exhibit a modest dielectric anisotropy, low viscosity and low absorption at the vicinity of $10.6 \mu\text{m}$ so that they are useful compounds for CO_2 laser beam steering application (see publication list #1). However, their nematic range is somewhat too narrow. We have formulated a ternary mixture consisting of 17 wt% PTTP-2F, 47 wt% PTTP-4F, and 36 wt% PTTP-8F. The threshold voltage of this ternary mixture was measured to be $1.3 V_{\text{rms}}$. However, its nematic range is from 55 to 81.7°C which is too narrow for many applications. Thus, some asymmetric PTTP-nm homologs are still needed in order to lower the melting temperature to below -20°C .

2.2 Tolanes

Some fluoro and difluoro tolanes were synthesized (by Prof. Hsu's group) and their physical properties evaluated. Their phase transition temperature, dielectric and optical properties are described in the following sections.

2.2.1 Fluoro Naphthylene Tolanes



where $X=\text{H}$ or F , and their associated compounds are abbreviated as NTP-n0F, and NTP-n0FF, respectively. Table 2 shows some physical properties of these compounds. Owing to the shorter conjugation length and increased lateral molecular width of the naphthylene ring, the Δn and $\Delta\epsilon$ of these compounds are all smaller than the diphenyl-diacetylene compounds listed in Table 1. In addition, the melting point of these naphthylenic tolanes is rather high and

nematic range is narrow so that they are not so attractive as PTPP-nF homologs for practical applications.

Table 2 Phase transition temperatures (in °C), Δn (at 23°C, $\lambda=589$ nm), $\Delta\epsilon$ (23°C, 1 kHz sine waves) and ΔH (in kcal/mol) of the fluoro-naphthylene tolanes. Here K, N and I stand for crystalline, nematic and isotropic phase, respectively. () means monotropic transition.

LCs	Phase Transition (°C)	Δn	$\Delta\epsilon$	ΔH
NTP-30F	K 122.0 N 129.5 I			6.66
NTP-40F	K 110.7 N 134.0 I			6.66
NTP-50F	K 104.9 N 123.0 I			5.05
NTP-60F	K 97.2 N 124.3 I	0.24	5.47	5.50
NTP-80F	K 93.8 N 117.5 I			8.92
NTP-30FF	K 117.9 I			7.21
NTP-40FF	K (69.9) N 92.0 I			6.10
NTP-50FF	K 74.5 N 85.4 I			4.29
NTP-60FF	K 73.1 N 88.2 I	0.21	9.19	4.43
NTP-80FF	K (73.8) N 87.2 I			9.54

2.2.2 Fluorinated Cyclohexane Tolanes

To widen nematic range while preserving a large $\Delta\epsilon$, fluorinated cyclohexane tolanes have been considered. Their structure is shown as following:



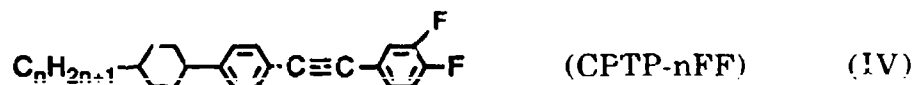
The phase transition temperature, Δn , $\Delta\epsilon$ and ΔH of the CPTP-nF compounds are listed in Table 3. From Table 1, the short-chain homolog CPTP-2F shows a wide nematic range, a modest Δn and a very small ΔH . The dielectric anisotropy of these fluoro tolanes is about 4. Moreover, these tolanes possess a relatively low viscosity. These compounds are excellent candidates for forming eutectic mixtures for the popular liquid crystal display device called super twist nematic (STN) displays where the required Δn is in the 0.15 to 0.20 range.

Table 3 Physical properties of the CPTP-nF homologs.

LCs	Phase Transition (°C)	Δn	$\Delta\epsilon$	ΔH
CPTP-2F	K 81.7 N 162.2 I			3.64
CPTP-3F	K 97.8 N 191.8 I			4.39
CPTP-4F	K 82.5 S _G 96.2 N 183.9 I			4.12
CPTP-5F	K 85.8 S _G 91.8 N 187.5 I			5.30
CPTP-6F	K 74.5 S _A 97.6 N 180.5 I	0.17	4.06	6.34
CPTP-7F	K 62.2 S _A 89.4 N 185.7 I			6.99

2.2.3 Difluoro Cyclohexane Tolanes

To further enhance $\Delta\epsilon$, some difluoro cyclohexane tolanes are considered:



Results are listed in Table 4. Generally speaking, the difluoro tolane shows a lower melting temperature, lower Δn but higher $\Delta\epsilon$ than the corresponding monofluoro tolane. From Table 4, a longer chain length does not necessarily lead to a lower melting temperature. For example, CPTP-2FF shows a relatively low melting point, wide nematic range, small ΔH and the lowest viscosity among its homologs. Thus, CPTP-2FF is the most attractive candidate in this series.

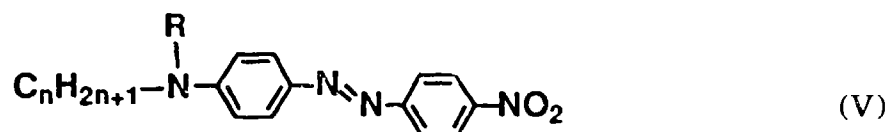
Table 4 Physical properties of the CPTP-nFF homologs.

LCs	Phase Transition (°C)	Δn	$\Delta\epsilon$	ΔH
CPTP-2FF	K 63.8 N 120.2 I			3.42
CPTP-3FF	K 91.4 N 145.7 I			6.23
CPTP-4FF	K 73.4 N 144.1 I			5.32
CPTP-5FF	K 81.2 N 155.0 I			5.30
CPTP-6FF	K 65.6 N 141.5 I	0.15	5.82	6.34
CPTP-7FF	K 54.6 N 147.5 I			7.19

2.3 Liquid Crystal Dyes

In collaboration with Prof. B. M. Fung of the Oklahoma University, we have discovered a series of dyes which exhibit mesogenic phases. These LC dyes possess a relatively low heat fusion enthalpy, low melting point and low viscosity. Thus, their solubility to most LC hosts is excellent. The dielectric anisotropy of these LC dyes is huge ($\Delta\epsilon \sim 40$) due to the presence of a strong on-axis dipole moment. Adding a few percent of such dye into a LC host greatly enhances the Δn , and lowers the threshold voltage of the mixture. However, the viscosity of the LC-dye system also increases in proportion to the dye concentration.

The structure of the new LC dyes we studied is shown below:



Here $\text{R} = \text{H}$ or CH_3 , and n is the number of the carbon atoms. Table 5 shows the phase transition temperatures of the nitro-azo-benzene dyes we obtained. From Table 5, we see that several dyes exhibit a mesogenic phase. In particular, the C-5 dye (with $\text{R} = \text{H}$ and $n = 5$) shows a melting point of about 85°C and a relatively small ΔH . Thus, its solubility to most commercially available LC host mixtures would be very good. In a solubility test, we found that the C-5 dye is soluble to E-7 (Merck) LC mixture as high as 30% which is about ten times higher than a typical commercial dye. For a longer side chain length (larger n), smectic-A phase appears. However, the melting point does not drop too noticeably.

It is surprising to note that by simply replacing R with a methyl group, the mesogenic phase no longer exists (c.f. last 3 rows in Table 5). Moreover, the melting point increases by about 20 degrees as compared to their corresponding compounds with $\text{R} = \text{H}$. The detailed physical mechanisms responsible for the observed phase transition are not yet clear. However, the results listed in Table 5 imply that the hydrogen bonding between these molecules increases the short range interactions at the liquid state. As a result, mesogenic phase appears. Although the dyes with $\text{R} = \text{CH}_3$ exhibit no mesogenic phase, they can still be used as dopants for enhancing the $\Delta\epsilon$, except for a lower concentration.

Table 5 Phase transition temperatures (in °C) and heat fusion enthalpy (ΔH in kcal/mol) of the nitro-azo-benzene dyes. Here K, S_A, N and I stand for crystalline, smectic-A, nematic and isotropic phase, respectively. () means monotropic transition.

R	n	Phase transitions	ΔH
H	4	K 109.1 I	6.55
H	5	K (75.5) N 84.6 I	5.79
H	6	K 85.7 N 86.2 I	7.82
H	7	K (69.7) S _A (79.4) N 86.1 I	7.32
H	8	K (68.2) S _A 81.9 N 85.4 I	8.10
H	9	K 76.0 S _A 85.6 N 86.9 I	9.44
H	10	K 84.3 S _A 89.0 I	9.69
H	11	K 90.7 S _A 93.3 I	10.10
H	12	K 101.1 I	11.39
H	14	K (93.3) S _A 98.8 I	13.30
CH ₃	5	K 102.1 I	5.40
CH ₃	6	K 119.0 I	8.55
CH ₃	7	K 112.4 I	---

Polarized absorption spectra of C5 are measured in a LC host ZLI-2359 (Merck) and the results are shown in Fig.1. The absorption peaks at about 460 nm and its dichroic ratio is 5.7. Due to the low viscosity of the C5 dye, useful application in the guest-host effect is foreseeable.

Fig.2 shows the temperature dependent dielectric constants of a binary mixture of the C5 (57 wt%) and C6 (43 wt%) dyes, designated as M56. At $T_r=0.95$, $\Delta\epsilon$ of M56 is 37. The large $\Delta\epsilon$ of these LC dyes results from their extraordinarily strong dipole moment due to the amino-nitro intramolecular charge transfer. The NO₂ group acts as an acceptor that induces electron flow from the benzene ring. On the other hand, the (C_nH_{2n+1})NH group acts as an electron donor which produces an opposite charge flow. This push-pull effect has been used frequently for designing molecules for nonlinear optics application. A large $\Delta\epsilon$ leads to a low threshold voltage (V_{th}) which is defined as: $V_{th} = \pi [K_{11}/\Delta\epsilon]^{1/2}$ where K_{11} is the splay elastic constant.

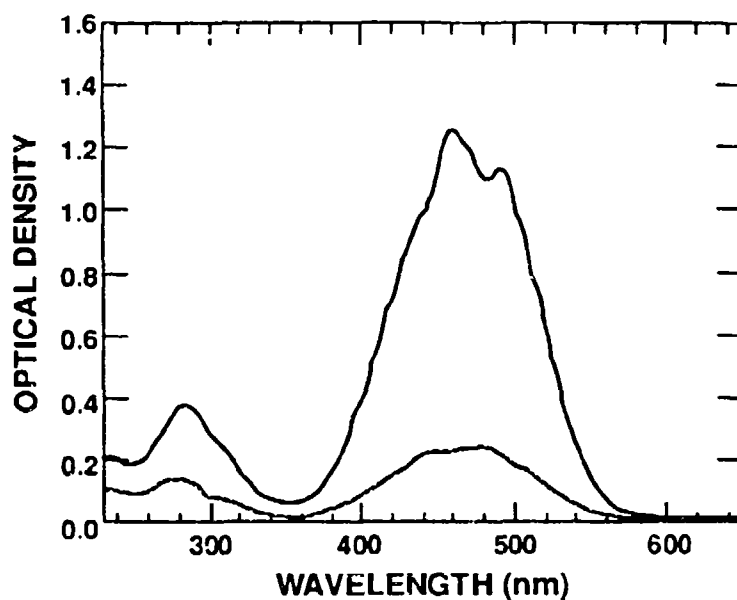


Fig.1 Polarized absorption spectrum of 1% C5 LC dye dissolved in ZLI-2359 vs ZLI-2359 without dye. Cell thickness is 6 μm . $T_r=0.868$. Solid and dashed lines are for extraordinary and ordinary rays, respectively.

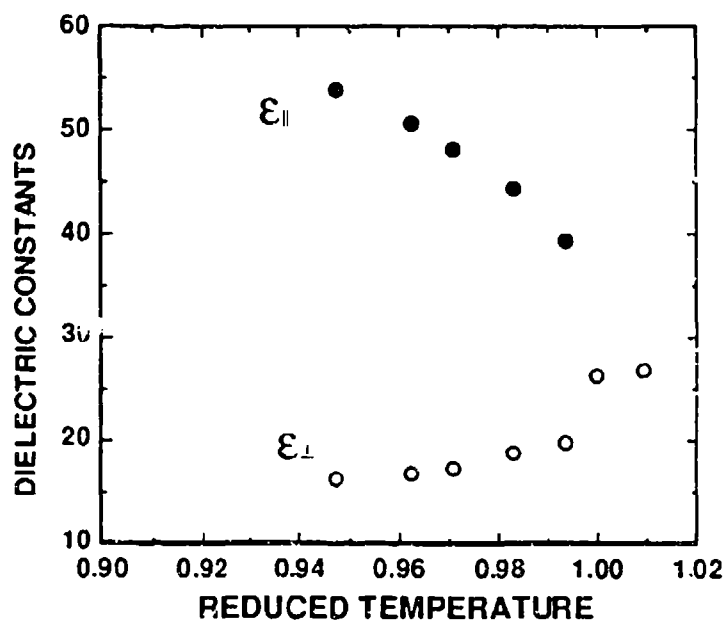


Fig.2 Reduced-temperature-dependent dielectric constants of the binary LC dye mixture (M56) at 1 kHz sine wave frequency.

Due to the large $\Delta\epsilon$ of C5 dye, doping also enhances the $\Delta\epsilon$ of the dye-doped E7 system linearly. This is shown in the right hand side of Fig.3. On the left hand side, the concentration effect on the visco-elastic coefficient is depicted. Again, as dye concentration increases, γ_1/K_{11} increases linearly. However, this increase is considered modest as compared to a commonly used dye, such as anthraquinone type (Merck). From Fig.3, a 5% C5 dye merely increases γ_1/K_{11} by 15% which is about one order of magnitude smaller than the anthraquinone dye.

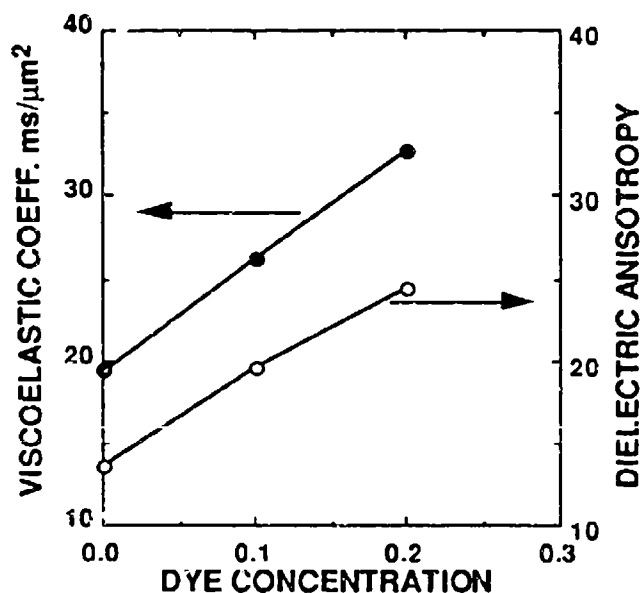


Fig.3 Dye (C5) concentration effect on visco-elastic coefficient (left) and dielectric anisotropy (right) at $T = 23^\circ\text{C}$. LC host is E7.

The huge $\Delta\epsilon$ of these new LC dyes is particularly attractive for mixing with nonpolar LCs. Table 6 shows some properties of the experimental mixture AF-7 which consists of 5% C5 dye, 47.5% PTP-24 and 47.5 % PTP-36. We found that by merely adding 5% of the C5 dye to the nonpolar PTP binary mixture, the threshold voltage drops from 3.5 to 1.7 V_{rms} while the visco-elastic coefficient increases by less than 15% at $T=23^\circ\text{C}$.

Table 6 Physical properties of the AF-7 mixture. Here n_e and n_o are measured at $\lambda=589\text{ nm}$ and $T=23^\circ\text{C}$.

Nematic Range	n_e	n_o	ϵ_{\parallel}	ϵ_{\perp}	γ_1/K_{11} (23 $^\circ\text{C}$)	V_{th}
7.9 to 93.9 $^\circ\text{C}$	1.886	1.530	6.17	2.87	22.8 ms/ μm^2	1.7 V_{rms}

3.0 EUTECTIC MIXTURES

During the course of this contract, we have formulated several experimental eutectic mixtures and delivered two mixtures to Raytheon Research Laboratory for testing their laser beam steering device. The figure-of-merit of our mixture is generally about 3-4 times higher than the commonly used commercial mixture E44 (Merck) at room temperature. Here, we briefly describe the physical properties of a mixture, designated as AF-5, we developed.

A. Composition

The compositions of the AF-5 mixture we formulated are listed in Table 7.

Table 7 Compositions of the AF-5 mixture

LC	wt%
PTTP-24	40.8
PTTP-36	41.5
PTTP-2F	3.0
PTTP-4F	8.3
PTTP-8F	6.4

B. Nematic Range

The nematic range of AF-5 was measured to be from -3 to 93 °C by the differential scanning calorimetric method.

C. Threshold Voltage

In the AF-5 mixture, the nonpolar dialkyl PTTP homologs are still dominant due to their favorable heat fusion enthalpy. The polar PTTP-nr² compounds make a limited contribution to enhancing the dielectric anisotropy of the mixture because of their low percentage in the composition. The threshold voltage of AF-5 was measured to be 2.4 V_{rms} at 23 °C and 1 kHz sine wave frequency.

D. Birefringence

Wavelength-dependent birefringence of AF-5 was measured by the scanning wavelength method at T=23 °C and results are compared with E44 as shown in Fig.4. The filled circles in Fig.5 represent experimental data for AF-5 and open circles for E44. As wavelength increases, Δn decreases gradually and saturates

in the IR region. From Fig.4, the birefringence of AF-5 remains as high as 0.3 at $\lambda=1 \mu\text{m}$, which is about 35 % higher than that of E44. At $10.59 \mu\text{m}$, the Δn of AF-5 was measured by the scanning voltage method to be 0.29 at $T=23^\circ\text{C}$.

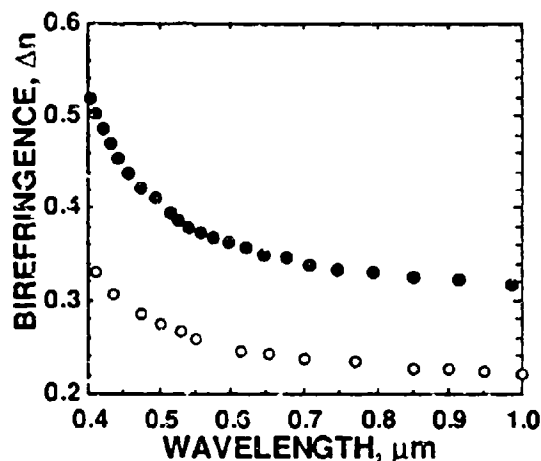


Fig.4 Wavelength-dependent birefringence of AF-5 (filled circles) and E44 (open circles) at $T=23^\circ\text{C}$.

Temperature-dependent Δn of AF-5 was measured at $\lambda = 0.633 \mu\text{m}$ using a HeNe laser beam. Results (filled circles) are shown in Fig.5. Also included in Fig.5 are the experimental results of E44 and E7. The clearing point of E44 is 100°C and E7 is 60°C . As temperature increases, Δn decreases gradually. A more pronounced effect takes place when the temperature approaches the clearing point.

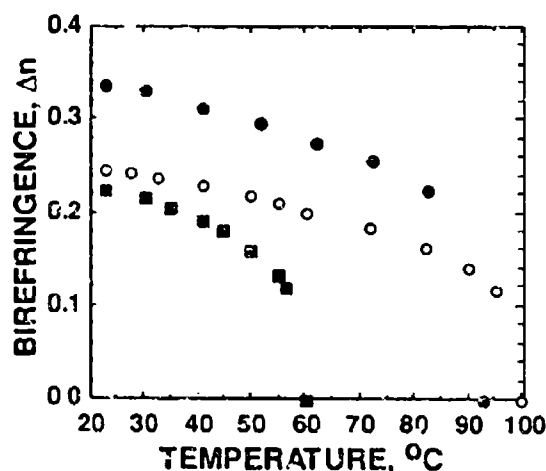


Fig.5 Temperature dependent Δn of AF-5 (filled circles), E44 (open circles) and E7 (squares) at 633 nm

D. Visco-elastic coefficient (γ_1/K_{11})

Although raising temperature causes an undesirable decrease in Δn , it also lowers the visco-elastic coefficient dramatically. Temperature-dependent visco-elastic coefficient of AF-5 (filled circles) and E44 (open circles) are depicted in Fig.6. At room temperature, the γ_1/K_{11} of AF-5 is nearly two times lower than that of E44 and 40% lower than E7. This is not surprising; the cyano compounds are known to possess a higher viscosity than the corresponding fluoro ones. As temperature increases, the γ_1/K_{11} of both mixtures decrease and begin to saturate at different temperatures. This is because both viscosity and elastic constant decrease with increasing temperature, but at a different rate. Beyond 75 °C, the visco-elastic coefficient of AF5 and E44 mixtures becomes nearly the same. Thus, the easiest way to achieve a high speed operation of a LC modulator is to operate the LC device at high temperature. The general problems for high temperature operation of a LC device are in its thermal instability and bulky heating apparatus.

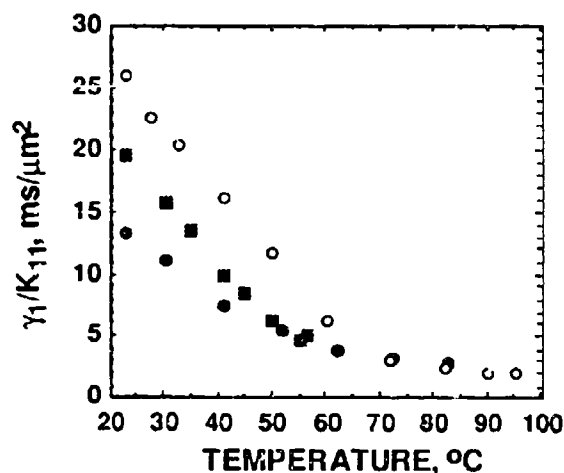


Fig.6 Temperature-dependent visco-elastic coefficient of AF5 (filled circles), E44 (open circles) and E7 (squares).

E. Figure-of-Merit

The figure of merit (FM) of a LC cell is defined as:

$$FM = K_{11}\Delta n^2/\gamma_1$$

which takes into account both the phase change and response time of a LC device is calculated from the results shown in Figs.5 and 6. At room temperature, the FM of AF-5 is about three times higher than that of E44 and E7. As temperature increases, the FM of both mixtures increases indicating that the gain in γ_1/K_{11} exceeds the loss in Δn^2 . From Fig.7, the FM exhibits a maximum at $\sim 70^\circ\text{C}$ for AF-5, $\sim 75^\circ\text{C}$ for E44 and $\sim 50^\circ\text{C}$ for E7. Above this temperature, γ_1/K_{11} has reached a saturation level whereas Δn^2 starts to decrease drastically with temperature. As a result, the FM declines sharply with increasing temperature.

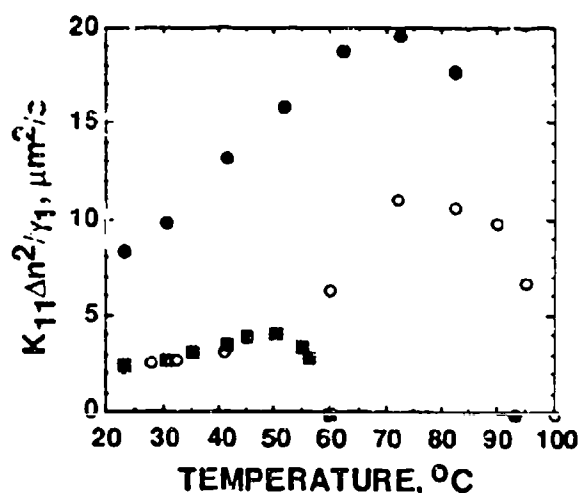


Fig.7 Temperature-dependent figure of merit of AF-5 (filled circles), E44 (open circles) and E7 (squares). The clearing point of AF-5, E44 and E7 is 93, 100 and 60 $^\circ\text{C}$, respectively. A HeNe laser, $\lambda=633$ nm, was used for these measurements.

4.0 SUMMARY

We have designed and synthesized several new diphenyl-diacetylene and tolane liquid crystals and new LC dyes. The asymmetric diphenyl-diacetylenes exhibit a low melting temperature, wide nematic range, high birefringence, small heat fusion enthalpy and low viscosity. They are excellent host materials for formulating eutectic mixtures for laser beam steering application. However, the dielectric anisotropy of these nonpolar compounds is too small. Polar dopants have to be added in order to enhance the dielectric anisotropy, or to reduce the operation voltage.

Two types of polar compounds have been developed for this purpose: 1. Fluoro diacetylenes and tolans, and 2. Nitro-azo-benzene dyes. The fluoro diphenyl-diacetylenes possess a high birefringence, low viscosity and modest dielectric anisotropy. Nevertheless, their nematic range is too narrow. They can be used as dopants only. The fluoro cyclohexane tolans exhibit a very wide nematic range. However, their birefringence is not so high as that of diphenyl-diacetylene. These tolans are particularly useful for visible display application employing the super-twisted nematic (STN) cell. The passive-matrix STN, together with the active matrix TN displays have become the main stream of the flat panel display technologies.

The nitro-azo-benzene dyes we studied exhibit a mesogenic phase with melting point at about 80°C. These liquid crystal dyes possess a high birefringence, excellent solubility, huge dielectric anisotropy and moreover, relatively low viscosity. Adding 5% of this dye to a binary asymmetric diphenyl-diacetylene mixture reduces the threshold voltage from 3.5 to 1.7 V_{rms}. The viscosity of this new dye is at least *one order of magnitude lower* than the commonly used commercial dyes. Thus, these dyes will be very useful in the guest-host cell. The guest-host cell can be used as a switchable dichroic polarizer which has great importance in the sensor protection technology. The Air Force Wright Laboratory has issued (June 1994) a Program Research & Development Announcement (PRDA) for developing switchable polarizers, in conjunction with the advanced tunable liquid crystal filter for sensor protection. We have submitted a proposal.

During the course of this program, we have prepared and delivered two experimental mixtures to Raytheon Research Laboratory (September 15, 1993) and AFOSR (March 15, 1994) for testing the laser beam steering devices developed by the Raytheon Company. The Raytheon's device is currently sponsored by the BMDO under a separate contract.

5.0 PUBLICATION LIST

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S. T. Wu, J. D. Margerum, M. S. Ho, and B. M. Fung, Appl. Phys. Lett.
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H. B. Meng, L. R. Dalton and S. T. Wu, Mol. Cryst. Liq. Cryst. (In press).
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Hungary, July 3-8, 1994; and manuscript submitted to Mol. Cryst. Liq.
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5. "Gas chromatography analysis of diphenyl-diacetylene liquid crystals",
E. Sherman, A. M. Lackner and S. T. Wu,
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